UV CURING: THE BASICS

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Introduction:

Ultraviolet light (UV) curing technology is one of the fastest growing technologies of today. Presumably a new technology, its beginnings actually date back to the late 1950's when epoxy acrylates were first used in coatings and adhesives. In the late 1960's, European manufacturers commercialized the usage of unsaturated polyester/styrene compositions. These coatings are still used as wood fillers and wood topcoats.[1] Acrylated urethanes, also developed in the 1960's, gained prominence in the 1970's.[2] In the early 1990's, UV curing accounted for approximately $400 million in sales of formulated products and is expected to grow at a rate of 15% to 25% annually.[3]

UV formulations are currently applied to a variety of substrates ranging from paper and wood to plastics and metal. Coatings, inks, adhesives and photopolymers are all common UV products available in today's market (figure 1). UV coatings can offer superior performance benefits, increased line speeds and low or zero volatile organic compound (VOC) emissions. When compared to conventional drying methods, less energy is required to cure UV products. The amount of heat generated while curing is also less, therefore; heat sensitive substrates can be coated. UV coatings are supplied in 100% solids, water based, solvent based, clear, pigmented and various gloss formulations.

UV curing can be described as a process that uses ultraviolet light to initiate the polymerization of a liquid material into a crosslinked material (figure 2). Hence the name "UV Curing."[4] Typically, the coating is applied to the substrate and passed through a curing unit. Exposure under the light source depends on the line speed and number of lamps present. Some exposure times are less than one second. The size of the curing unit is determined by the type of parts coated, but typically takes less floor space than a conventional finishing system. Various light sources can be used to initiate polymerization ranging from medium pressure mercury vapor lamps and electrodeless lamps, to xenon lamps and argon ion lasers. Most frequently used are the medium pressure mercury lamps and the electrodeless lamps. These lamps are placed over the conveyor and can be arranged to cure flat as well as multi-dimensional parts.

BASIC CHEMISTRY

The main components of a 100% solids UV formulation are: acrylated oligomers, mono and multifunctional monomers and photoinitiators. Oligomers are moderately low molecular weight resins that contribute to the overall properties of the coating, ink or adhesive. Most of the oligomers are based on the acrylation of different chemical structures. The acrylation process imparts unsaturation (C=C) to the two ends of the oligomer (figure 3). Table 1 describes the advantages, disadvantages and uses of commonly used oligomers:

Table 1

Oligomer	Advantages	Disadvantages	Uses
Polyesters	low viscosity, moderate cost	poor surface cure, slight yellowing	wood fillers, primers, and topcoats, inks, laminating adhesives plastic and paper coatings
Urethanes	toughness, flexibility, abrasion resistance, excellent weatherability (aliphatic), best overall qualities	highest cost yellowing (aromatic)	plastics coatings overprint varnishes, wood coatings, vinyl flooring
Epoxies	fast cure, good chemical resistance, hard films, economical, adhesion to metal, low in cost	yellowing	metal can coatings, paneling, adhesives, wood coatings

Monofunctional Monomers

Monofunctional monomers are low molecular weight materials that have one reactive group, usually a double bond (C=C). This double bond permits the monomer to react when exposed to UV light and become incorporated into the cured coating. Monofunctional monomers are used to lower the viscosity of the coating. Some monofunctional monomers aid in increasing flexibility and adhesion of the coating to the substrate. Examples of monofunctional monomers are 2-ethylhexyl acrylate and vinyl acetate (figure 4).

Multifunctional Monomers

Multifunctional monomers also function as diluents to reduce viscosity, but their most important function is to form links between the oligomer molecules and other monomers within the coating. The linking together of the oligomers and monomers creates a net-like effect imparting hardness, toughness, strength and adhesion to the cured coating. Examples of multifunctional monomers are: trimethylolpropane triacrylate (TMPTA) and hexanediol diacrylate (HDODA) (figure 5).

Monomer selection can "make or break" a formula. By choosing specific monomers, a formulator can vary the links formed during cure. For example, using a trifunctional monomer, with its three functional groups, will produce a coating with tighter crosslinking, i.e., a smaller net-like effect. The increased crosslink density will result in films with greater solvent resistance and hardness, but flexibility and elongation will be reduced. Since the majority of oligomers and monomers shrink during cure, choosing monomers known for their adhesion promoting properties will help minimize this effect. Elongation can be varied by both oligomer and monomer selection.

Photoinitiators

Photoinitiators are compounds added in small amounts to the coating (figure 6). When exposed to a specific wavelength of energy, the photoinitiator absorbs light and generates free radicals that initiate polymerization of the oligomers and monomers. The reaction caused by the free radicals occurs at the carbon-carbon double bonds.[5] The exact amount and type of photoinitiator used is based on the oligomer/monomer selection, film thickness, light source, and the atmosphere present when curing. Since the photoinitiator must be exposed to light to generate free radicals, any coated areas of the substrate not exposed to light will remain uncured. Free radical polymerization proceeds through the following steps:

1. **INITIATION - In the initiation stage, the photoinitiator absorbs the light energy and generates the free radicals.**

2. PROPAGATION AND CHAIN TRANSFER - This step involves the addition of the free radical to monomeric species. This is the most important step in the process and occurs hundreds of times for each individual occurrence of the other steps.[6]

The initiation process can only occur during exposure to the UV light source. Since any existing free radicals have very short life spans, all of the propagation reactions stop or greatly slow down when the coating is no longer under the light source. Consequently, the majority of the final product's properties are achieved. *Within minutes, a part can be prepped, sprayed, cured and packed for shipment.*

3. TERMINATION - Termination of the reaction occurs when: growing polymer sites react together, a reactive propagating species reacts with a less reactive species, the light source is removed, or in the presence of oxygen. Oxygen is a radical scavenger and will decrease the rate or stop polymerization. The effect will be most noticeable at the surface of the coating; surface properties can range from a decrease in mar resistance to very tacky or wet. There is also a decrease in solvent resistance and long term weathering. Some common practices of overcoming oxygen are through the use of amine synergists, waxes, higher intensity light source and to use a nitrogen blanket (figure 7).

LIGHT SOURCE

For the photoinitiator to absorb light energy, the correct light source must be used. The most frequently used light source is the medium pressure mercury vapor lamp. This lamp emits wavelengths from about 200 to 420 nanometers. Some mercury vapor lamps are doped to change the spectral output so that specialized photoinitiators can be used or to decrease the amount of infrared emissions. Others are used to achieve effects such as gloss reduction. Another type of lamp is the electrodeless lamp. This lamp relies on microwaves to activate the lamp. The spectral output of the electrodeless lamp is similar to the mercury vapor lamp and can also be doped to shift the spectra. Benefits of electrodeless lamps over mercury vapor lamps are: longer life, much shorter warm-up time, highly efficient UV output and less IR output.[7]

The above mentioned lamps are commonly available in wattages ranging from 200 watts per inch (wpi) to 600 wpi. It is equally important to chose the correct wattage for the application. The degree of cure varies with the lamp selection. A 600 wpi lamp may over cure the coating, a 400 wpi lamp may properly cure the coating, and a 200 wpi lamp may under cure the coating. However, using two 200 wpi lamps, or increasing line speed and using one 600 wpi lamp may or may not give the same results as a 400 wpi lamp. This phenomenon is due to the chemistry of the coating and the substrate on which the coating is applied.

Other materials such as surfactants, pigments and inhibitors are added to improve appearance and/or properties. Table 2 lists some frequently used raw materials, characteristics, approximate percentages used and results expected from each material.[8]

TABLE 2

INGREDIENT	CHARACTERISTIC	APPROX. PERCENT USED	RESULT FROM USE
Oligomers	•Epoxy Acrylates (Hard Resins)	0 - 100	•Stiff, hard to brittle, low extension, adhesion on non-porous substrates
	•Urethane Acrylates (Hard and Soft Resins)	0 - 100	•Flexible to stiff and/or brittle, low to high extension, adhesion, excessive shrinkage
	•Polyesters	0 - 100	•Soft and flexible to hard
	•Blends of Hard and Soft Acrylates	5/95 - 95/5	•Intermediate depending on combination used
Monomers	•Monofunctional	0 - 80	•Lower viscosity, improved adhesion to loss of cure and properties
	•Multifunctional	0 - 80	•Increase bonds, crosslink density, adhesion, to stiff, tough or brittle
Other Resins	Reactive and Nonreactive	0 - 15	Plasticize, reduce cost, enhance adhesion
Photoinitiator	Free Radical and Cationic	.25 - 5	Increase/decrease cure speed, decrease shelf life
Stabilizers	Heat, light, antioxidants, formulation	20-200 PPM	Increase shelf life, inhibit precure, improve weathering, prevent property loss
Surfactants	•Dispersants, wetting agents	0 - 2	•Disperse and wet pigments and fillers, prevent phase separation
	•Flow Modifier	0 - 5	•Flow and leveling
	•Defoamers	0- 1.5	•Reduce foam, bubbles
Pigments, Fillers, Flatting agents		0 - 45	Impart color, increase viscosity, decrease cure and stability, decrease cost
Adhesion Promoter		0 - 5	Improve adhesion
Dual Cure Additive		0 - 3	aid in cure

Ultraviolet - Cationic Curing

Another form of curing using ultraviolet light is cationic curing. In cationic curing, a specific form of photoinitiator, when exposed to light, can initiate polymerization through an ionic reaction rather than a free radical reaction (figure 8). This type of chemistry also requires different resins and diluents. Cyclic aliphatic epoxides are the most common resins used. The unique aspect of cationic curing is that polymerization continues after the coating has been exposed to light. A post bake is often used to continue the polymerization. While oxygen does not interfere with cationic curing, humidity can have a significant effect. Some uses of cationic coatings are protective coatings on metal can ends, printing inks on metal, specialty adhesive and sealant systems, and for the potting and encapsulation of electronic components.[9]

BASIC APPLICATION CONSIDERATIONS

- **Initial start up costs. Startup costs can range from new equipment purchases to altering existing equipment. Electrical, storage facilities, and employee training are other startup costs.**

- **Shape of substrate. Acrylated UV coatings cure only where the coating "sees" the light. A part with sharp angles may not be able to be cured. Some parts may require a 3-D type unit to cure all angles.**

- **Variety of parts to be coated. Varying the size and shape of the parts to be coated month to month may require additional line configuration options.**

- **Type of substrate to be coated. Some substrates are difficult to adhere to and require additional processing.**

- **Fully pigmented systems are hard to cure. Pigmentation interferes with light absorption by the photoinitiator.**

APPLICATION AND CURING PARAMETERS

The following list describes some of the parameters that must be addressed when designing a UV cure line.

1. **Application: Spray, Rollcoat, Gravure, etc. How should the coating, adhesive or ink be applied?**
2. **Line Speed: What line speed is required for production? Overprint coatings can be cured at line speeds of 1000 fpm or more, while coating wood products may require line speeds of only 10 fpm. The formulation must be geared to the line speed required.**
3. **Substrate pretreatment: Does the substrate need to be sanded, prewashed or otherwise pretreated before coating?**

4. Cure in Air or Inert: In addition to air, some substrates interfere with curing and require a nitrogen blanket to achieve thorough curing of the coating.
5. Flash off Tunnel or IR unit: Some 100% solids formulations require a short prebake before cure to achieve maximum flow. Some UV curables contain solvent that may need to be flashed before cure, and cationic coatings require a post bake.
6. Lamp type: What type of lamp best cures the coating?
7. Let UV equipment supplier test chemistry to determine type and size of equipment to be specified.
8. Lab or pilot tests are always necessary before decision is made to purchase equipment.

For example, a simple line set up for plastic parts may include a prewash station, the actual coating line, a short heated tunnel or IR unit to flash off solvents or aid in flow of 100% solids, the curing chamber, and exit to the packing line. This type of line is usually more economical and takes up less space than a conventional line. Typically, the coating's manufacturer will discuss the system with the UV equipment manufacturer to determine the best line configuration and lamps required for optimum cure. Often, trial runs are held at the equipment manufacturer's facility to fine tune the complete coating/curing system.

HEALTH AND SAFETY

Just as solvents, catalysts and isocyanates used in many coatings require additional safety when handling, so do UV curables. Ingredients in these formulations can cause skin sensitization and burns. Peering into the UV curing chamber can cause extreme pain to the eyes and the possible formation of cataracts as well as severe skin burns. However, the energy associated with UV curing is not sufficient to penetrate into the body and interact with the tissue to produce any dramatic effects such as cancer (figure 9).[10]

Typical personal protective equipment such as nitrile rubber gloves, safety glasses or goggles and safety shoes protect employees who work with liquid UV coatings (figure 10).

Where employees may be exposed to UV light, special UV glasses, forearm sleeves and inexpensive suits are available. Respirators are recommended if exposed to spray mist.

Since UV coatings do not cure unless exposed to light, any spills on shoes or clothing must be immediately removed and discarded. Skin exposed to liquid coatings should immediately be washed with soap and water. Solvents should never be used under any circumstances to clean skin.

Conclusion

Ultraviolet cured coatings, inks and adhesives offer low or no VOC's, low energy requirements and fast cure alternatives to conventional systems. The acrylation

of the oligomers and monomers allows these materials to be cured when exposed to specialized wavelength bulbs. UV coatings are available in a wide variety of formulations including fillers, sealers, and topcoats in various glosses. Some can be pigmented. UV coatings, inks and adhesives provide properties similar to or exceeding their conventional counterparts. Less space and energy are required when using UV coatings providing the end user with increased production and a decrease in manufacturing cost. Since the curing process produces less heat *than conventional* systems, *heat* sensitive substrates can be easily be coated. With an expected growth rate of 15% to 25% annually, UV coatings, inks and adhesives have found a niche in the Finishing Industry.

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[9] Vara, Fulvio, et al.

[10] Vara, Fulvio, et al.

Uses of UV Curing Technology

- Dental Bonding
- Adhesives
- Magnetic Recording Media
- Metal Coatings
- Optical Fiber Coatings
- Paper and Board Coatings
- Coatings for Rigid and Flexible Plastics
- Leather Coatings
- Wood Coatings
- Photopolymer Printing Inks
- Textiles

Figure 1

Ultraviolet Free Radical Reaction

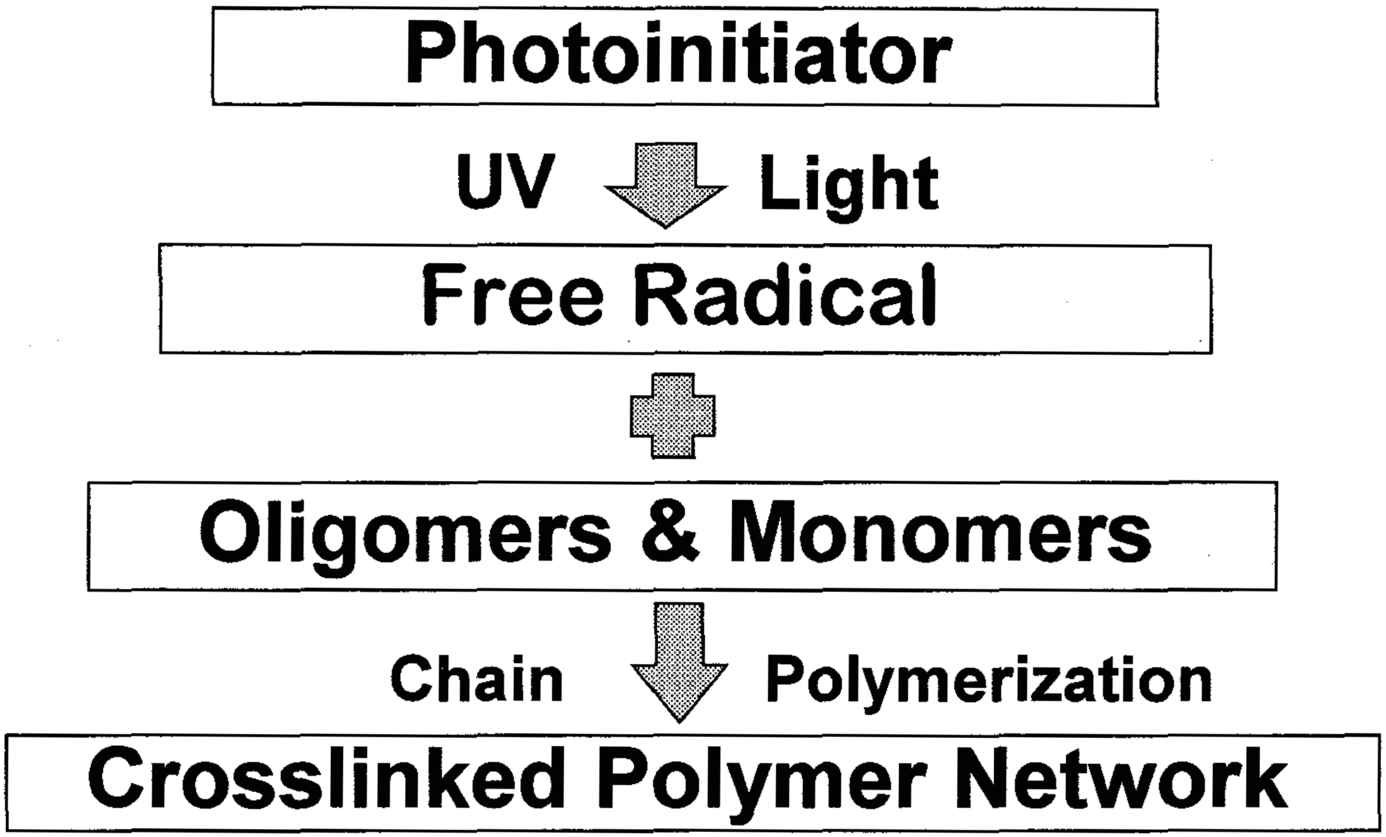
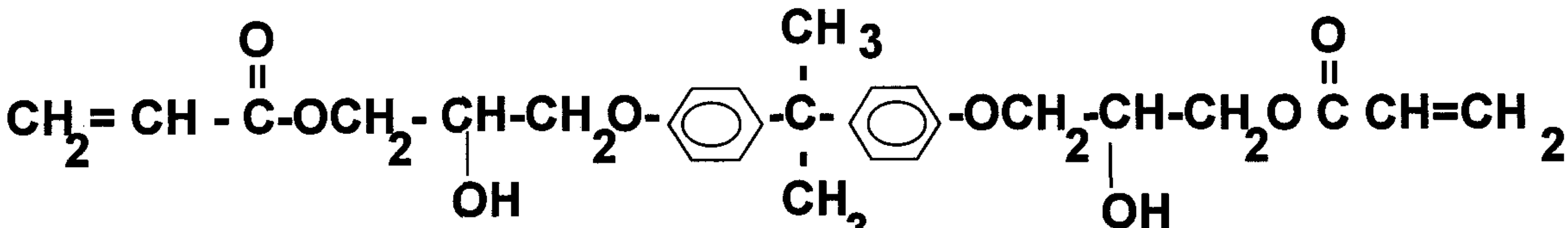
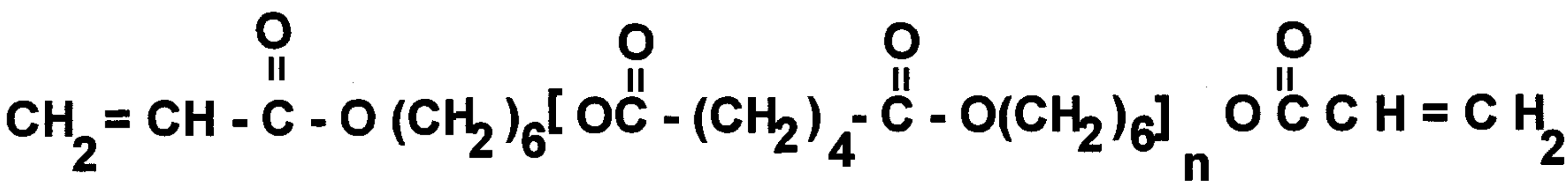


Figure 2

Acrylated Oligomers



Acrylated Epoxy



Acrylated Polyester

Figure 3

Monofunctional Monomers

$$CH_2=CH-\overset{O}{\overset{\|}{C}}-OCH_2-\underset{C_2H_5}{\underset{|}{CH}}-CH_2CH_2CH_2CH_3$$

2 - Ethylhexyl Acrylate

$$CH_2=CH-O\overset{O}{\overset{\|}{C}}-CH_3$$

Vinyl Acetate

Figure 4

Multifunctional Monomer

$$CH_2=CH-\underset{\underset{O}{\|}}{C}-O-CH_2CH_2CH_2CH_2CH_2CH_2-O-\underset{\underset{O}{\|}}{C}-CH=CH_2$$

1 , 6 - Hexanediol Diacrylate (HDODA)

Figure 5

Photoinitiator

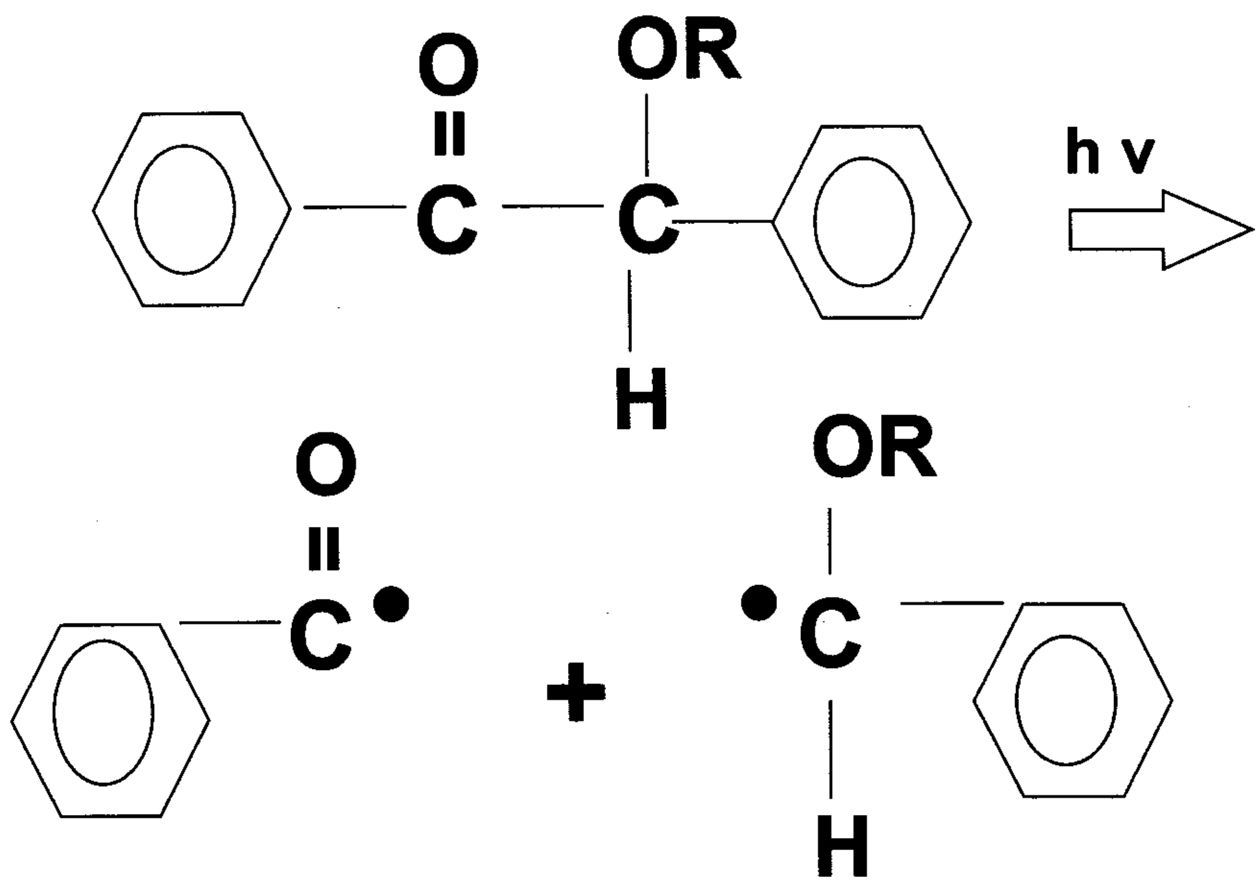


Figure 6

Free Radical Polymerization

Acrylates

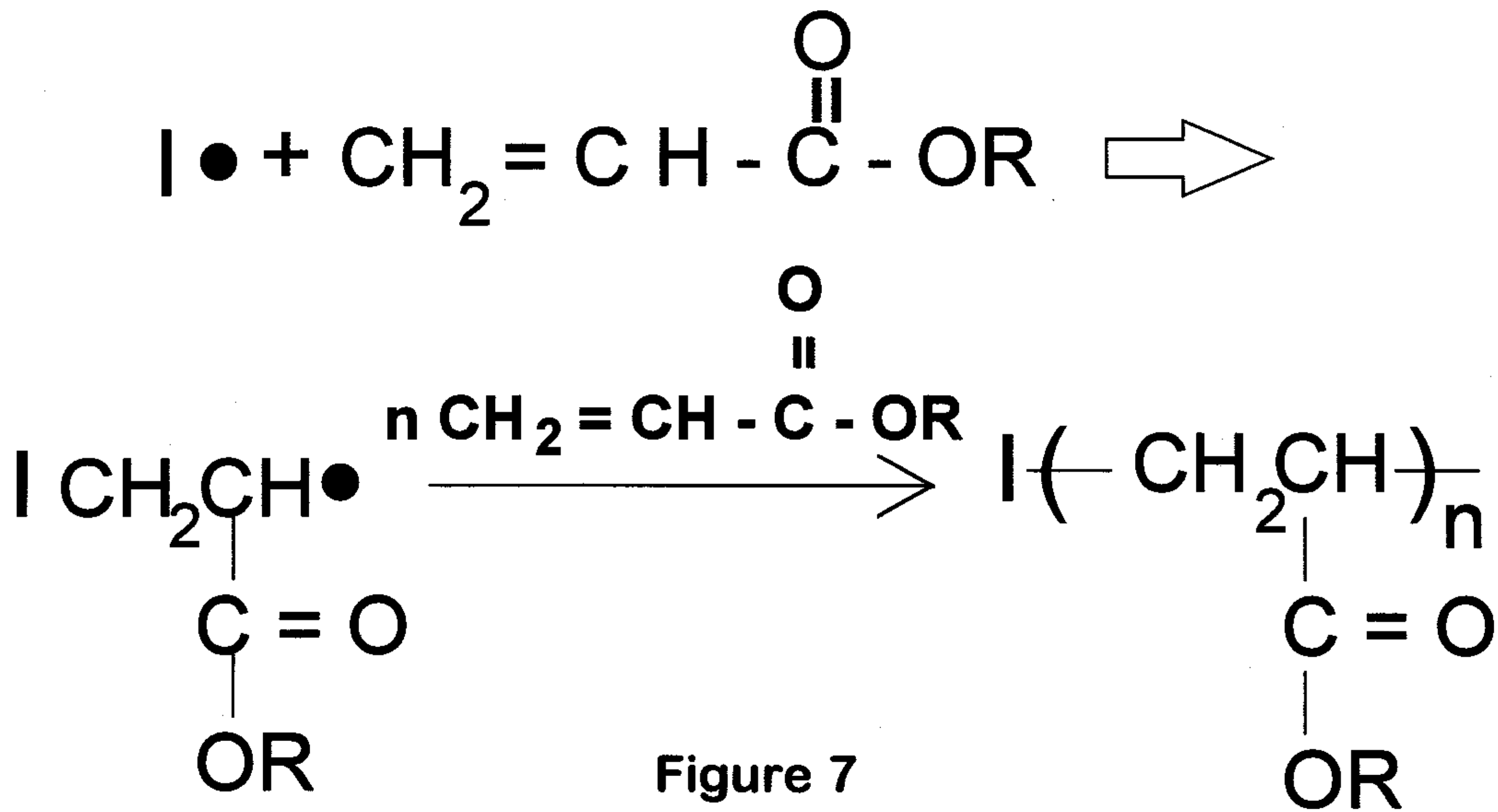


Figure 7

Cationic Polymerization

$$Ar_3\overset{\oplus}{S}\,X^{\ominus} \xrightarrow{h\nu} H^{\oplus} + Ar_2S + Ar^{\bullet} + X^{\ominus}$$

$$H^{\oplus} + n\ \underbrace{CH_2 - CHR}_{\text{bridged by } O} \longrightarrow \left(CH_2 - \underset{\displaystyle R}{\underset{|}{CH}} - 0 \right)_n H$$

Figure 8

717

Precautions

Skin or Eye Exposure to Ultraviolet Light Coatings and Exposure to Processor Lights

May Cause or Aggravate the Following:

- Dermatitis
- Blistering of skin
- Rashes
- A severe sunburn
- Burning and tearing of eyes

Figure 9

General Safety Guidelines

- Wear Gloves
- Wear Goggles
- Wash Spills off Skin With Soap and Water
- Wash Hands Before Eating and Using the Washroom
- Never Use Solvent to Clean Skin
- Immediately Remove Contaminated Shoes and Clothing

Figure 10

•NOTES•

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